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Synthesis, structure and electrochemical properties of triarylamine bridged dicobaltdicarbon tetrahedrane clusters.[†]

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[†] Dedicated to Professor R.D. Adams, on the occasion of his 65th birthday, and in recognition of his outstanding contributions to the development and promotion of cluster chemistry.

Abstract

The reaction of $[Co_2(CO)_6(dppm)]$ (**1**) with the ethynyl substituted triarylamines $[N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)(C_6H_4Me\text{-}4)_2]$ (**2**) or $[N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)_2(C_6H_4Me\text{-}4)]$ (**3**) affords $[\{Co_2(CO)_4(dppm)\}\{\mu\text{-}(Me_3SiC_2\text{-}4\text{-}C_6H_4)N(C_6H_4Me\text{-}4)_2\}]$ (**4**) or a mixture of $[Co_2\{\mu\text{-}Me_3SiC_2\text{-}4\text{-}C_6H_4N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)(C_6H_4Me\text{-}4)\}(CO)_4(dppm)]$ (**5**) and $[\{Co_2(CO)_4(dppm)\}_2\{\mu\text{-}(Me_3SiC_2\text{-}4\text{-}C_6H_4)_2N(C_6H_4Me\text{-}4)\}]$ (**6**), respectively. A combination of electrochemical measurements in different electrolytes, and IR and NIR spectroscopic studies of these compounds, which feature both organometallic and organic redox active groups,

indicates that the cluster centres are oxidised at significantly less positive potentials than the triarylamine moieties. Reaction of **6** with one or two equivalents of [Fe(η-$C_5H_4COMe)Cp]PF_6$ gives [**6**][$PF_6]_n$ (n = 1, 2), which are best described in terms of cluster-localised oxidation processes. Despite the presence of the substantial differences in the first and second cluster based oxidations in **6** (up to 220 mV in CH_2Cl_2 / 0.1M [NBu_4][BAr^F_4]), there is little ground state delocalisation between the cluster centres through the triarylamine bridge. The stabilisation of [**6**]$^+$ with respect to disproportionation can be attributed to electrostatic effects.

Keywords

Cobalt-alkyne; electron transfer; electrochemistry; spectroelectrochemistry; mixed valence

Introduction

The study of complexes in which a ligand bridges two or more organic, inorganic or organometallic redox active moieties is in the midst of a significant renaissance [1-4]. These systems are ideal candidates for the study of intramolecular electron transfer processes [5-7], which in turn underpin applications in catalysis [8], energy science [9, 10] and molecular electronics [11, 12] whilst also illustrating fine details of electronic structure arising from the often unexpected redox activity of the supporting or bridging ligands [13-17]. Whilst the considerable majority of studies in this area have focussed on bis(monometallic) complexes in which two metal centres are linked through a (usually π-conjugated) bridging ligand [18, 19], systems derived from organic electrophores [20] and cluster systems [21] have not been overlooked. Within this range of molecular scaffolds, cluster systems offer some appealing aspects

not so easily introduced using organic or mono-metallic systems, such as the capacity to act as an electron-sink and often offering IR active probe groups (e.g. CO ligands) which are sensitive to the electron density at the cluster core and can be used to probe intra and inter molecular electron transfer processes on a relatively fast timescale [22-26]. In addition, the well-developed synthetic chemistry of cluster complexes permits the simple design of candidate systems, with cluster cores introduced either as redox active probe groups [27- 31] or directly within the bridging entity [32-41].

Dicobaltdicarbon tetrahedrane clusters of general form $[Co_2(\mu\text{-}RC_2R')(CO)_{6-n}L_n]$ are conveniently prepared from reactions of $[Co_2(CO)_8]$ and alkynes, $RC{\equiv}CR'$, with carbonyl ligand exchange reactions with ligands L (usually phosphines and phosphites). Alternatively, initial reaction of $[Co_2(CO)_8]$ with L may be used to prepare the substituted derivatives $[Co_2(CO)_{8-n}L_n]$ which undergo further reaction with alkynes to give the tetrahedrane products [42]. This simple reaction sequence, coupled with the capacity to readily tune the electrochemical behaviour of the resulting Co_2C_2 clusters through ligand substitution reactions and relatively simple IR ν(CO) spectra has led to several investigations of the redox chemistry and electron transfer behaviour in ligand bridged species based on these moieties [43-45]. For example, following initial electrochemical studies by Osella [46], the Otago group have used a combination of electrochemical and spectroelectrochemical methods to show that oxidation of $[\{Co_2(CO)_4(dppm)\}_2(\mu\text{-}PhC_2C_2Ph)]$ in which two tetrahedrane clusters are linked by a C-C single bond, gives rise to a mono-cation in which the cluster centres are in identical electronic environments on the IR timescale [47]. Interpolation of other π-conjugated moieties between the cluster centres gives rise to less strongly coupled to decoupled systems [48-50], with results from electrochemical

studies being consistent with a significant contributions from both through-space and through-bond effects to the stabilisation of the one-electron redox products in some cases [51].

We have previously taken advantage of the relatively simple synthetic protocols, ease of crystallisation, characteristic ν(CO) spectra and electrochemical response of $[Co_2(\mu\text{-}RC_2R')(CO)_4(dppm)]$ clusters and used the Co_2C_2 cluster core as an electronic, spectroscopic, and redox-active auxiliary in studies of bridge-mediated electronic interactions [53-55]. In the present study we have been drawn to related complexes in which Co_2C_2 clusters are linked by a redox active triarylamine group. In addition to offering possibilities to investigate the bridge-mediated electronic coupling of organic and organometallic electrophores, the triarylamine group offers an interesting topology when employed as a bridging ligand, capable of promoting linear conjugation between up to three remote sites through the central nitrogen atom [56-59]. Here we describe the results of our initial investigations, and give details of the synthesis, structure, electrochemical and spectroelectrochemical response of $[\{Co_2(CO)_4(dppm)\}_2\{\mu\text{-}(Me_3SiC_2\text{-}4\text{-}C_6H_4)_2N(C_6H_4Me\text{-}4)\}]$ (**6**). The experimental results, together with those from the related mono-cluster complex $[\{Co_2(CO)_4(dppm)\}\{\mu\text{-}(Me_3SiC_2\text{-}4\text{-}C_6H_4)N(C_6H_4Me\text{-}4)_2\}]$ (**4**), support a description of $[\mathbf{6}]^{n+}$ in terms of a localised electronic structure, with the radical confined to a single cluster redox centre in the case of n = 1.

Experimental

General conditions. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Reaction solvents were purified and dried using

an Innovative Technology SPS-400, and degassed before use. No special precautions were taken to exclude air or moisture during work-up. The compounds $[Co_2(CO)_6(dppm)]$ [60], $[Pd_2(dba)_3]$ [61], 1,1'-bis(diphenylphosphino)ferrocene (dppf) [62], $[PdCl_2(PPh_3)_2]$ [63] $[Pd(PPh_3)_4]$ [64], $[N(C_6H_4Br\text{-}4)(C_6H_4Me\text{-}4)_2]$ [65], $[NC_6H_4Br\text{-}4)_2(C_6H_4Me\text{-}4)]$ [66], $[N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)(C_6H_4Me\text{-}4)_2]$ [67] and $[N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)_2(C_6H_4Me\text{-}4)]$ [66] were prepared by the literature routes, or minor modifications as detailed below. Other reagents were purchased and used as received.

The NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer from deuterated chloroform solutions and referenced against residual protio solvent resonances ($CHCl_3$: ^1H 7.26 ppm; ^{13}C 77.0 ppm) or external phosphoric acid. IR spectra were recorded using a Thermo 6700 spectrometer from CH_2Cl_2 solutions in a cell fitted with CaF_2 windows. MALDI -mass spectra of organometallic complexes were recorded using Autoflex II TOF/TOF mass spectrometer with a 337 nm laser. Samples in CH_2Cl_2 (1 mg / ml) were mixed with a matrix solution of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in a 1:9 ratio, with 1 μl of mixture spotted onto a metal target prior to exposure to the MALDI ionization source. Organic compounds were analysed by GC-EI(+) mass spectrometry using a Trace GCMS instrument. Elemental analyses were performed by technical staff at the Department of Chemistry, Durham University.

Electrochemical analyses were carried out using an EcoChemie Autolab PG-STAT 30 potentiostat, with platinum working, platinum counter and platinum pseudo reference electrodes, from solutions in CH_2Cl_2 containing 0.1 M supporting electrolyte, ν = 100

mV s^{-1}. The decamethylferrocene / decamethylferrocenium (FcH^*/FcH^{*+}) couple was used as an internal reference for potential measurements such that the FcH/FcH^+ couple falls at 0.00 V (FcH^*/FcH^{*+} = –0.48 V) [68]. Spectroelectrochemical measurements were made in an OTTLE cell of Hartl design [69], from CH_2Cl_2 solutions containing 0.1 M $[NBu_4]PF_6$ electrolyte. The cell was fitted into the sample compartment of the Thermo 6700 or Thermo Array UV-Vis spectrophotometer, and electrolysis in the cell was performed with a PGSTAT-30 potentiostat. In ^{13}C NMR assignments, the various C_6H_4 and C_6H_5 rings are denoted Ar-cluster (for the phenylene ring pendent to the Co_2C_2 cluster core), Ar-CH_3 (for the tolyl rings pendent to the amine N centre) and Ph for those rings associated with the dppm ligand. In cases where assignments were ambiguous, the term 'Ar' is used.

X-ray crystallography

Single crystal X-ray data were collected at 120 K on a Bruker SMART 6K (compounds **4** and **5**; graphite monochromator, $\lambda_{MoK\alpha}$, λ = 0.71073 Å) and at 100 K on a Bruker Proteum M rotating anode (compound **6**, focusing mirrors, $\lambda_{CuK\alpha}$, λ = 1.54178 Å) diffractometers equipped with Cryostream and Cobra (Oxford Cryosystems) cryostats respectively. The data for all compounds were corrected for absorption by multi-scan method using SADABS program [70]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using OLEX2 [71] and SHELX [72] software. All non-disordered non-hydrogen atoms were refined with anisotropic displacement parameters, atoms of disordered groups were refined isotropically with fixed SOF = 0.5. All H atoms were placed in the calculated positions and refined in "riding" mode. Crystallographic data and refinement parameters are listed in Table 1. Crystallographic data for the structures

have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 871097 - 871099.

Table 1 Crystal data and structure refinement for **4**-**6**

Compound	**4**	**5**	**6**
Empirical formula	$C_{54}H_{49}Co_2NO_4P_2Si$ x CH_2Cl_2	$C_{58}H_{55}Co_2NO_4P_2Si_2$ x CH_2Cl_2	$C_{87}H_{77}NO_8Si_2P_4Co_4$
Formula weight	1068.76	1150.94	1680.28
Temperature/K	120	120	100
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	10.0519(2)	13.4179(3)	12.5714(5)
b/Å	15.3922(3)	14.6648(3)	14.0341(6)
c/Å	18.5247(4)	15.7740(4)	24.9132(10)
α/°	72.071(10)	75.9950(10)	101.688(2)
β/°	79.906(10)	72.6230(10)	100.653(2)
γ/°	83.068(10)	83.1210(10)	102.245(2)
Volume/$Å^3$	2677.94(9)	2870.37(11)	4085.4(3)
Z	2	2	2
$\rho_{calc}mg/mm^3$	1.325	1.332	1.366
μ/mm^{-1}	0.845	0.814	7.712
F(000)	1104	1192	1732
Reflections	50506	47964	14939

collected			
Independent reflections, R_{int}	14880, 0.0357	15262, 0.0374	9317, 0.0368
Data / restraints / parameters	14880/0/604	15262/0/609	9317/0/866
Goodness-of-fit on F^2	1.047	1.061	1.050
Final R_1 indexes [$I \geq 2\sigma(I)$]	0.0432	0.0585	0.0532
Final wR_2 indexes [all data]	0.1307	0.1707	0.1485

Syntheses

Preparation of $[Co_2(CO)_6(dppm)]$ (1) A Schlenk flask was charged with degassed toluene (60 ml), to which $[Co_2(CO)_8]$ (5.0 g, 14.6 mmol) was added and the resulting solution stirred whilst treated with dppm (5.61 g, 14.6 mmol) in several small portions at room temperature. The CO liberated after each addition was allowed to completely evolve prior to addition of the subsequent aliquot of diphosphine. The solution gradually became burnt orange in colour, and a bright orange precipitate became evident after approximately 30 minutes of reaction. The solution was allowed to stir for several hours, during which time copious amounts of product precipitated from the reaction solution. When adjudged complete, the solution was filtered to give $[Co_2(CO)_6(dppm)]$ as a free-flowing microcrystalline orange powder in essentially

quantitative yield (ca. 9.7 g), identical with that prepared by the literature method [60].

Preparation of [NH(C_6H_4Me-4)$_2$] To an oven dried flask was added dry toluene (50 ml) and the solvent rigorously degassed three times using the freeze-pump-thaw technique. To the degassed solvent, *para*-toluidine (2.23 g, 20.8 mmol), 4-iodotoluene (5.00 g, 22.9 mmol), [$Pd_2(dba)_3$] (0.19 g, 0.21 mmol), dppf (0.35 g, 0.63 mmol) and sodium *tert*-butoxide (3.00 g, 31.2 mmol) were added and the mixture stirred at reflux for 20 h. The mixture was cooled, filtered and the solvent removed *in vacuo*. The residue was purified by silica column chromatography eluting with hexane increasing to a hexane:acetone (95:5) mixture. The eluent was concentrated *in vacuo* to 5 ml and the precipitated white solid collected and washed with cold hexane (2 x 5 ml) to give [NH(C_6H_4Me-4)$_2$] (2.77 g, 68 %). ^{1}H NMR: δ 2.30 (s, 6H, CH_3), 5.51 (s, 1H, NH), 6.95 (d, J = 8 Hz, 4H, Ar) 7.07 (d, J = 8 Hz, 4H, Ar). ^{13}C NMR: δ 20.6 (CH_3), 117.9 (Ar_o), 129.8 (Ar_m), 130.2 (Ar_p), 141.1 (Ar_i). ES-MS(+) (*m/z*): 197.2 $[M+H]^+$.calculated for ($C_{14}H_{15}N$) 197.12 m/z, found 197.20 m/z.

Preparation of [N(C_6H_4Br-4)(C_6H_4Me-4)$_2$] To an oven dried flask was added dry toluene (50 ml) and the solvent rigorously degassed three times using the freeze-pump-thaw technique before [NH(C_6H_4Me-4)$_2$] (2.38 g, 12.0 mmol), 1-bromo-4-iodobenzene (3.76 g, 13.2 mmol), [$Pd_2(dba)_3$] (0.11 g, 0.12 mmol), dppf (0.20 g, 0.36 mmol) and sodium *tert*-butoxide (1.74 g, 18.1 mmol) were added and the mixture stirred at reflux for 60 h. The mixture was cooled, filtered and the solvent removed *in vacuo*. The residue was treated with petroleum ether (30 ml) and the persistent solid removed by filtration, and the precipitate washed with petroleum ether (2 x 30 ml).

The combined organic solutions were concentrated *in vacuo* to ca. 10 ml, which upon standing deposited a white precipitate. The precipitate was collected by filtration, and washed with cold petroleum ether (5 ml) to give [$N(C_6H_4Br\text{-}4)(C_6H_4Me\text{-}4)_2$] (2.84 g, 69 %). ^{1}H NMR: δ 2.32 (s, 6H, CH_3), 6.90 (d, J = 9 Hz, 2H, Ar), 6.98 (d, J = 8 Hz, 4H, Ar), 7.08 (d, J = 8 Hz, 4H, Ar), 7.28 (d, J = 9 Hz, 2H, Ar). ^{13}C NMR: δ 20.8 (CH_3), 113.6 ($Ar_{p'}$), 123.9 (Ar_o), 125.0 ($Ar_{o'}$), 130.3 (Ar_m), 131.9 ($Ar_{m'}$), 132.9 (Ar_p), 145.0 (Ar_i), 147.4 ($Ar_{i'}$). ESI-MS(+) (*m/z*): 351.1 $[M+H]^+$.

Preparation of [$N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)(C_6H_4Me\text{-}4)_2$] (2) To an oven dried flask was added dry triethylamine (75 ml) and the solvent rigorously degassed three times using the freeze-pump-thaw technique. To the degassed solvent [$N(C_6H_4Br\text{-}4)(C_6H_4Me\text{-}4)_2$] (1.80 g, 5.12 mmol), $HC{\equiv}CSiMe_3$ (0.85 ml, 6.15 mmol), [$PdCl_2(PPh_3)_2$] (0.18 g, 0.25 mmol) and copper(I) iodide (0.02 g, 0.13 mmol) were added and the mixture stirred under reflux for 17 h. The mixture was cooled, filtered and the solvent removed under high vacuum. The residue was treated with hexane (30 ml) and the precipitated solid removed by filtration and washed with hexane (2 x 10 ml). The solvent was removed from the combined filtrates *in vacuo* and the residue purified by silica column chromatography in hexane increasing polarity to a hexane:CH_2Cl_2 (8:2) mixture. The solvent was removed *in vacuo* to leave a yellow oil that solidifies on standing, affording [$N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)(C_6H_4Me\text{-}4)_2$] (1.37 g, 73 %). ^{1}H NMR: δ 0.25 (s, 9H, $SiMe_3$), 2.33 (s, 6H, CH_3), 6.90 (d, J = 9 Hz, 2H, Ar), 6.98 (d, J = 8 Hz, 4H, Ar), 7.08 (d, J = 8 Hz, 4H, Ar), 7.28 (d, J = 9 Hz, 2H, Ar). ^{13}C NMR: δ 0.00 ($SiMe_3$), 14.0 (CH_3), 92.5 ($\underline{C}{\equiv}CSiMe_3$), 105.6 ($C{\equiv}\underline{C}SiMe_3$) 114.8 ($Ar_{p'}$), 120.8 ($Ar_{o'}$), 125.1 ($Ar_o$), 129.9 ($Ar_m$), 132.7 ($Ar_{m'}$), 133.1 ($Ar_p$), 144.6 ($Ar_i$), 148.3 ($Ar_{i'}$). ESI-MS(+) (*m/z*): 370.3 $[M+H]^+$.

Preparation of [N(C_6H_4Br-4)$_2$(C_6H_4Me-4)] In oven dried glassware purged with nitrogen, dry toluene (50 ml) was degassed by freeze-pump-thaw methods. To this solvent was added *para*-toluidine (0.54 g, 5.04 mmol), 1-bromo-4-iodobenzene (2.97 g, 10.5 mmol), [$Pd_2(dba)_3$] (0.05 g, 0.05 mmol), dppf (0.08 g, 0.15 mmol) and sodium *tert*-butoxide (1.35 g, 14.0 mmol). The reaction was heated to reflux for 36 hours, after which time the solution was allowed to cool to room temperature before being poured into water. The resulting suspension was extracted with dichloromethane (3 x 30 ml) and the combined organic phases washed with water (3 x 40 ml), dried over magnesium sulphate, filtered and the solvent removed to produce a black residue. The crude product was purified by column chromatography on silica (hexane) to give [N(C_6H_4Br-4)$_2$(C_6H_4Me-4)] as a white crystalline solid (1.37 g, 66 %). ^{1}H NMR: δ 2.32 (s, 3H, CH_3), 6.91 (d, 4H, J = 8 Hz, Ar-Br), 6.97 (d, 2H, 8 Hz, Ar-CH_3), 7.09 (d, 2H, 8 Hz, Ar-CH_3), 7.32 (d, 4H, 8 Hz, Ar-Br). ^{13}C NMR: δ 21.2 (CH_3), 115.3 ($Ar_{p'}$), 125.2 ($Ar_{o'}$), 125.5 (Ar_o), 130.6 (Ar_m), 132.6 ($Ar_{m'}$), 134.2 (Ar_p), 144.6 (Ar_i), 147.0 ($Ar_{i'}$). GC-EI(+) MS (*m/z*): 417.0 (100 %).

Preparation of [N(C_6H_4-4-C≡C$SiMe_3$)$_2$(C_6H_4Me-4)] (3) In oven dried glassware purged with nitrogen, dry triethylamine (40 ml) was degassed by freeze pump thaw methods. The reagents [N(C_6H_4Br-4)$_2$(C_6H_4Me-4)] (1.00 g, 2.41 mmol), $Me_3SiC{\equiv}CH$ (3.4 ml, 240.0 mmol), [$Pd(PPh_3)_4$] (0.08 g, 0.07 mmol) and copper iodide (0.01 g, 0.07 mmol) were added to the solvent and the solution heated at reflux point for 18 hrs. The solution was allowed to cool to room temperature and the precipitated ammonium salts removed by filtration. The solvent was removed from the filtrate *in vacuo*, and the remaining brown oil purified by flash chromatography on

silica [hexane - 3:10 CH_2Cl_2/hexane gradient] to produce a yellow oil which solidified under high vacuum (0.66 g, 60%). ^{1}H NMR: δ 0.23 (s, 18H, $SiMe_3$), 2.33 (s, 3H, CH_3), 6.94 (d, 4H, J = 8 Hz, Ar), 6.97 (d, 2H, J = 8 Hz, Ar), 7.09 (d, 2H, J = 8 Hz, Ar), 7.31 (d, 4H, J = 8 Hz, Ar). ^{13}C NMR: δ 0.4 ($SiMe_3$), 21.2 (CH_3), 93.0 ($\underline{C}$≡C$SiMe_3$), 106.0 (C≡$\underline{C}$$SiMe_3$), 115.2 ($Ar_{p'}$), 121.3 ($Ar_{o'}$), 125.5 ($Ar_o$), 130.3 ($Ar_m$), 133.2 ($Ar_{m'}$), 133.6 ($Ar_p$), 145.0 ($Ar_i$), 148.8 ($Ar_{i'}$). GC-EI(+) MS (*m/z*): 451.2. IR (CH_2Cl_2): ν(C≡C) 2105, ν(C-H) 3295, 3311 cm^{-1}.

Reaction of [N(C_6H_4-4-C≡C$SiMe_3$)(C_6H_4Me-4)$_2$] with [$Co_2(CO)_6$(dppm)] The reagents [N(C_6H_4-4-C≡C$SiMe_3$)(C_6H_4Me-4)$_2$] (0.11 g, 0.30 mmol) and [$Co_2(CO)_6$(dppm)] (0.20 g, 0.30 mmol) were added to dry degassed toluene (12 ml) and heated to 80 °C under nitrogen for two hours. The solvent was removed and the resulting residue purified by preparative TLC using hexane and acetone (70:30). A brown band was collected, the solvent removed and X-ray quality crystals of [{$Co_2(CO)_4$(dppm)}{μ-(Me_3SiC_2-4-C_6H_4)N(C_6H_4Me-4)$_2$}] (**4**) (0.15 g, 51 %) were obtained from the slow diffusion of methanol into a CH_2Cl_2 solution. ^{1}H NMR: δ 0.36 (s, 9H, $SiMe_3$), 2.32 (s, 6H, CH_3), 3.28 – 3.37 (m, 2H, dppm), 6.83 – 7.30 (m, 32H, 20H Ph + 12H Ar). ^{13}C NMR: δ 1.2 (s, $SiMe_3$), 21.2 (s, CH_3), 36.6 (t, $^1J_{CP}$ = 20 Hz, dppm), 88.7 (t, $^2J_{CP}$ = 9 Hz, C_2SiMe_3), 106.0 (t, $^2J_{CP}$ = 9 Hz, C_2SiMe_3), 123.4 (s, *o/m*-Ar cluster), 124.4 (s, *o/m*-Ar-CH_3), 128.2 (pseudo t, $^3J_{CP}$ = 5 Hz, *m*-PPh_2), 128.7 (pseudo t, $^3J_{CP}$ = 5 Hz, *m*-PPh_2), 129.4 (s, *p*-PPh_2), 129.9 (s, *p*-PPh_2), 130.2 (s, *o/m*-Ar-CH_3), 130.8 (s, *o/m*-Ar cluster), 131.0 (pseudo t, $^2J_{CP}$ = 6 Hz, *o*-PPh_2), 132.3 (s, *p*-Ar-CH_3), 133.0 (pseudo t, $^2J_{CP}$ = 6 Hz, *o*-PPh_2), 135.1 (pseudo t, $^1J_{CP}$ = 16 Hz, *i*-PPh_2), 136.7 (pseudo t, $^3J_{CP}$ = 3 Hz, *p*-Ar cluster), 139.4 (pseudo t, $^1J_{CP}$ = 25 Hz, *i*-PPh_3), 145.6 (s, *i*-Ar-CH_3), 146.1 (s, *i*-Ar cluster), 203.6 (s, CO), 207.7 (s, CO). ^{31}P

NMR: δ 35.1. MALDI(+)-MS (*m/z*) : 871.1 $[M-4CO]^+$. IR (CH_2Cl_2): ν(CO) 2017m, 1989s, 1961m, 1942w cm^{-1}. Anal. Calcd ($C_{54}H_{49}Co_2NO_4P_2Si$): C, 65.91; H, 5.02; N, 1.42. Found: C, 66.03; H, 5.22; N, 1.36 %.

Reaction of $[N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)_2(C_6H_4Me\text{-}4)]$ with $Co_2(CO)_6(dppm)$ The reagents $[N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)_2(C_6H_4Me\text{-}4)]$ (0.06 g, 0.14 mmol) and $[Co_2(CO)_6(dppm)]$ (0.20 g, 0.30 mmol) were added to dry degassed toluene (12 ml) and heated to 80 °C under nitrogen overnight. The solvent was removed and the resulting residue purified by preparative TLC using hexane and acetone (70:30). Two major bands were observed and collected. The first band was identified as $[Co_2\{\mu\text{-}Me_3SiC_2\text{-}4\text{-}C_6H_4N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)(C_6H_4Me\text{-}4)\}(CO)_4(dppm)]$ (**5**) (0.044 g, 31 %) and the second band as $[\{Co_2(CO)_4(dppm)\}_2\{\mu\text{-}(Me_3SiC_2\text{-}4\text{-}C_6H_4)N(C_6H_4Me\text{-}4)\}]$ (**6**) (0.086 g, 38 %). X-ray quality crystals of each complex were obtained from slow diffusion of methanol into a CH_2Cl_2 solution. $[Co_2\{\mu\text{-}Me_3SiC_2\text{-}4\text{-}C_6H_4N(C_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)(C_6H_4Me\text{-}4)\}(CO)_4(dppm)]$ (**5**): ^{1}H NMR: δ 0.25 (s, 9H, $SiMe_3$), 0.37 (s, 9H, $SiMe_3$), 2.35 (s, 3H, CH_3), 3.23 – 3.40 (m, 2H, dppm), 6.86 – 7.32 (m, 32H, 20H Ph + 12H Ar). ^{13}C NMR: δ 0.3 (s, $SiMe_3$), 1.1 (s, $SiMe_3$), 21.1 (s, CH_3), 36.4 (t, $^1J_{CP}$ = 20 Hz, dppm), 88.8 (t, $^2J_{CP}$ = 10 Hz, C_2SiMe_3), 93.1 (s, $C{\equiv}CSiMe_3$), 105.3 (t, $^2J_{CP}$ = 10 Hz, C_2SiMe_3), 105.7 (s, $C{\equiv}CSiMe_3$), 115.3 (s, *p*-Ar-CH_3), 121.4 (s, *o/m*-Ar), 124.6 (s, *o/m*-Ar), 125.7 (s, *o/m*-Ar), 128.0 (pseudo t, $^3J_{CP}$ = 5 Hz, *m*-PPh_2), 126.5 (pseudo t, $^3J_{CP}$ = 5 Hz, *m*-PPh_2), 129.3 (s, *p*-PPh_2), 129.6 (s, *p*-PPh_2), 130.3 (s, *o/m*-Ar), 130.7 (s, *o/m*-Ar), 130.8 (pseudo t, $^2J_{CP}$ = 6 Hz, *o*-PPh_2), 132.7 (pseudo t, $^2J_{CP}$ = 6 Hz, *o*-PPh_2), 133.0 (s, *o/m*-Ar), 133.8 (s, *p*-Ar), 134.9 (pseudo t, $^1J_{CP}$ = 17 Hz, *i*-PPh_2), 138.4 (unresolved pseudo triplet, *p*-Ar cluster), 139.1 (pseudo t, $^1J_{CP}$ = 24 Hz, *i*-PPh_2), 144.5

(s, *i*-Ar-CH_3), 144.8 (s, *i*-Ar cluster), 148.4 (s, *i*-Ar), 203.2 (s, CO), 207.3 (s, CO). ^{31}P NMR: δ 36.0. MALDI(+)-MS (*m/z*): $[M-4CO]^+$. IR (CH_2Cl_2): ν(C≡C) 2149w; ν(CO) 2016m, 1988s, 1961m, 1941w cm^{-1}. Anal. Calcd ($C_{58}H_{55}Co_2NO_4P_2Si_2$): C, 65.34; H, 5.20; N, 1.31. Found: C, 64.97; H: 5.16; N, 1.29 %.

$[\{Co_2(CO)_4(dppm)\}_2\{\mu\text{-}(Me_3SiC_2\text{-}4\text{-}C_6H_4)_2N(C_6H_4Me\text{-}4)\}]$ (**6**): ^{1}H NMR: δ 0.39 (s, 18H, $SiMe_3$), 2.35 (s, 3H, CH_3), 3.32 – 3.37 (t, 4H, dppm), 6.88 – 7.26 (m, 52H, 40H Ph + 12H Ar). ^{13}C NMR: δ 1.2 (s, $SiMe_3$), 21.0 (s, CH_3), 36.2 (t, $^1J_{CP}$ = 20 Hz, dppm), 88.6 (t, $^2J_{CP}$ = 9 Hz, C_2SiMe_3), 105.9 (t, $^2J_{CP}$ = 8 Hz, C_2SiMe_3), 123.6 (s, *o/m*-Ar cluster), 125.0 (s, *o/m*-Ar-CH_3), 128.0 (pseudo t, $^3J_{CP}$ = 4 Hz, *m*-PPh_2), 128.5 (t, $^3J_{CP}$ = 4 Hz, *m*-PPh_2), 129.3 (s, *p*-PPh_2), 129.7 (s, *p*-PPh_2), 130.0 (s, *o/m*-Ar-CH_3), 130.6 (s, *o/m*-Ar cluster), 130.7 (pseudo t, $^2J_{CP}$ = 8 Hz, *o*-PPh_2), 132.8 (pseudo t, $^2J_{CP}$ = 6 Hz, *o*-PPh_2), 135.0 (pseudo t, $^1J_{CP}$ = 16 Hz, *i*-PPh_2), 137.0 (s, *p*-Ar cluster), 139.1 (pseudo t, $^1J_{CP}$ = 24 Hz, *i*-PPh_2), 145.2 (s, *i*-Ar-CH_3), 145.7 (s, *i*-Ar cluster), 203.4 (s, CO), 207.4 (s,CO). **p-Ar not observed / obscured.* ^{31}P NMR: δ 35.7. MALDI(+)-MS: 953.0 $[M-4CO-\{Co_2(CO)_4(dppm)\}]^+$]. IR ($CH_2Cl_2$): ν(CO) 2016m, 1989s, 1960m, 1942w cm^{-1}. Anal. Calcd ($C_{87}H_{77}Co_4NO_8P_4Si_2$): C, 62.17; H, 4.62; N, 0.83. Found: C, 62.10; H, 4.58; N, 0.83 %.

Results and Discussion

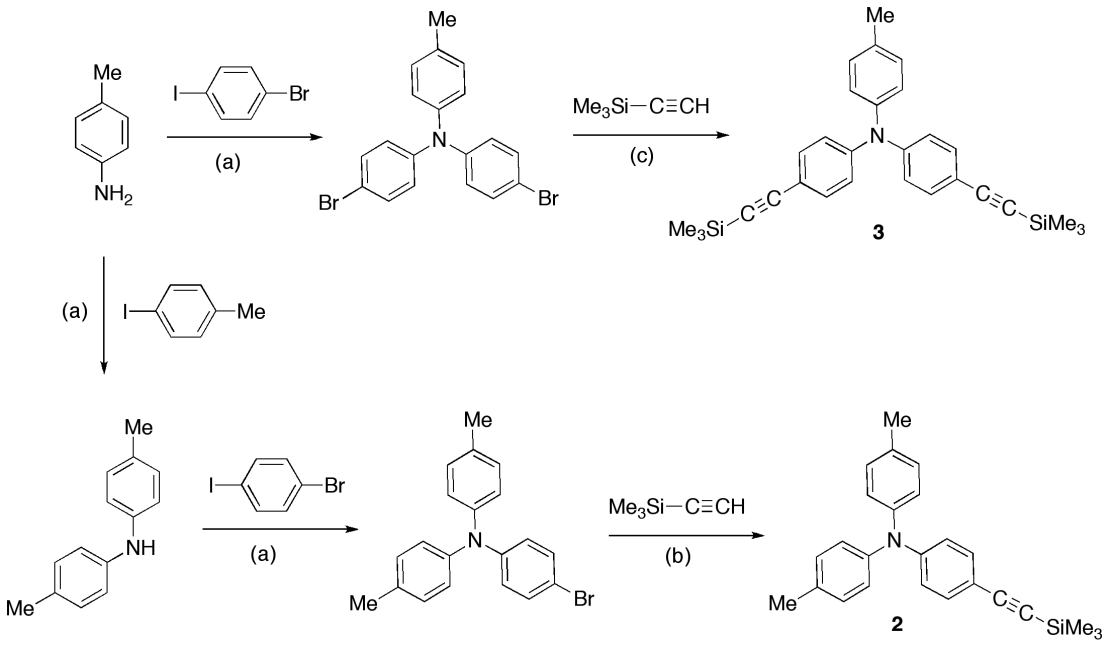
Synthesis Complexes of general form $[Co_2(\mu\text{-}RC_2R')(CO)_4(dppm)]$ are most conveniently prepared from thermal reactions of $[Co_2(CO)_6(dppm)]$ (**1**) with an alkyne. Compound **1** is usually prepared using the method of Chia and Cullen from the room temperature reaction of $[Co_2(CO)_8]$ and one equivalent of dppm in benzene, followed by chromatographic purification and crystallisation [60]. If the reaction is

carried out in toluene, compound **1** precipitates directly from the reaction mixture as a high purity powder and in essentially quantitative yield.

Triarylamines undergo one-electron oxidation processes to give radical cations, the chemical and thermodynamic stability (E^o) of which can be tuned through electronic and steric effects by variation in the substituents on the aryl groups [68], leading to extensive materials chemistry applications [73-77]. The redox activity of the triarylamine group, together with the simple synthetic chemistry associated with the preparation of such species, has prompted consideration of triarylamine based ligands **2** [67] and **3** [66] in organometallic chemistry.

The alkynes **2** and **3** were prepared from *para*-toluidene and di(tolyl)amine, respectively, through sequential Hartwig-Buchwald amination [78, 79] and Sonogashira cross-coupling [80] reactions (Scheme 1). There are numerous reports of the preparation of the ligand building block 4,4'-dimethyldiphenylamine, [$NH(C_6H_4Me\text{-}4)_2$], from arylation reactions of *para*-toluidine with 4-chloro [81-88], bromo- [89, 90] or iodo- [91] toluene; the material is also available commercially. We elected to employ a simple combination of readily available palladium source [$Pd_2(dba)_3$], supporting phosphine (dppf) and base (NaO^tBu) in a Hartwig-Buchwald based methodology to cross couple 4-iodotoluene with *para*-toluidene, which gave 4,4'-dimethyldiphenylamine in good (68%) yield in an experimentally convenient fashion. The same conditions were employed to selectively couple the iodo moiety in 1-bromo-4-iodobenzene to each of *para*-toluidene and 4,4'-dimethyldiphenylamine, which afforded the mono- and di-bromo substituted tertiary amines [$N(C_6H_4Br\text{-}4)(C_6H_4Me\text{-}4)_2$] and [$N(C_6H_4Br\text{-}4)_2(C_6H_4Me\text{-}4)$], respectively (Scheme 1). Alternate

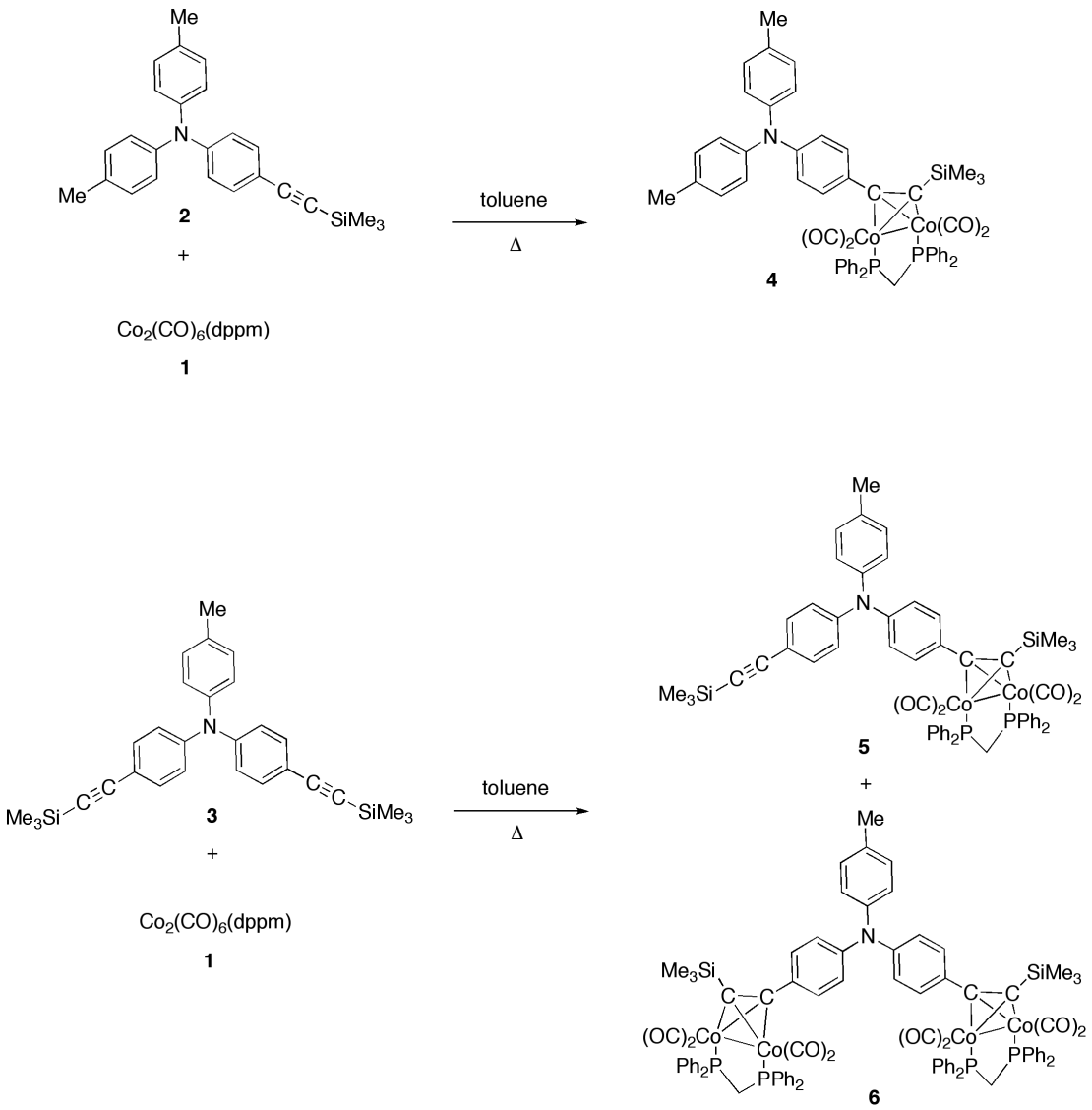
approaches in the literature to similar compounds include sequences of Ullmann couplings and bromination reactions [66] but we have found the application of the $[Pd_2(dba)_3]$ / dppf / NaO^tBu / toluene system to be a reliable and simple synthetic protocol.



Scheme 1. Preparation of the ligands **2** and **3**. Conditions: (a) $[Pd_2(dba)_3]$ / dppf / NaO^tBu / toluene / reflux; (b) $[PdCl_2(PPh_3)_2]$ / CuI / NEt_3 / reflux; (c) $[Pd(PPh_3)_4]$ / CuI / NEt_3 / reflux.

Subsequent reaction of **1** with **2** or **3** gave the anticipated Co_2C_2 clusters with pendant (**4**, **5**) or bridging (**6**) triarylamine groups (Scheme 2). The complexes were all readily identified by the usual combination of spectroscopic methods and microanalytical methods, and confirmed by single crystal X-ray diffraction. The IR ν(CO) spectra of all three complexes were essentially identical [**4** 2017m, 1989s, 1961m, 1942w; **5** 2016m, 1988s, 1961m, 1941w; **6** 2016m, 1989s, 1960m, 1942w cm^{-1}]. When these

data are compared with related systems such as $[Co_2(\mu\text{-}HC_2Ph)(CO)_4(dppm)]$ [ν(CO) 2027vs, 1999s, 1975s, 1956w cm^{-1}) $[Co_2(\mu\text{-}HC_2C_6H_4NMe_2)(CO)_4(dppm)]$ [ν(CO) 2023vs, 1995s, 1971s, 1952w cm^{-1}] and $[Co_2(\mu\text{-}Me_3SiC_2C{\equiv}C\{Ru(PPh_3)_2Cp\})(CO)_4(dppm)]$ [2004s, 1981vs, 1954s cm^{-1}] [92] the influence of the relatively strong electron donating triarylamine group on the cluster core in **4**, **5** and **6** is apparent. The carbon nuclei of the cluster cores in **4**, **5** and **6** are identified as triplets (J_{CP} ca. 9 Hz) near δ_c 89 and 106 ppm in each case, whilst the CO ligands give rise to resonances near δ_c 203 and 207 ppm. The dppm ligands give rise to singlets in the ^{31}P NMR spectra near δ_P 31 ppm. Together these IR and NMR data indicate the electronic environment of the clusters to be similar across the series. Other features of the triarylamine moiety and dppm ligands give rise to the expected resonances in the ^{1}H and ^{13}C spectra. Mass spectra obtained using MALDI methods display rather extensive fragmentation, with $[M–4CO]^+$ and, in the case of **6**, $[M–4CO–\{Co_2(CO)_4(dppm)\}]^+$, ions being predominant.



Scheme 2 The preparation of **4**, **5** and **6**

Molecular structures The molecular structures of **4** (Figure 1), **5** (Figure 2) and **6** (Figure 3) were confirmed by single crystal X-ray diffraction studies using crystals grown from slow diffusion of methanol into CH_2Cl_2 solutions of the complexes. Selected bond lengths, angles and torsions are summarised in the figure captions. The dppm ligands are disposed so as to minimise steric interactions with the $SiMe_3$ groups, while the triarylamine moieties exhibit the usual planar environment at N(1)

with the aryl rings disposed in a propeller arrangement. The N(1)-C(6) distances fall in the same range as found for the other N-C_{Ar} bonds in these complexes and $[N(C_6H_5)_3]$ (N-C_{Ar} = 1.408(7) - 1.427(6) Å across four independent molecules) [93]. The bond lengths around the C(3)-C(8) phenylene ring are typical for a *para*-substituted system, and display no significant quinoidal distortions. Within the Co_2C_2 tetrahedrane cluster core, the Co(1,3)-Co(2,4) bond lengths span a narrow range [2.4821(5) - 2.4933(10) Å], whilst the C(1)-C(2) distances are identical [1.350(2) (**4**); 1.351(4) (**5**); 1.351(6), 1.353(6) (**6**) Å] both of which are similar to those found in $Co_2(\mu\text{-}HC_2Ph)(CO)_4(dppm)$ [Co-Co 2.4873(3) Å; C-C 1.348(2) Å] [92]. It must therefore be concluded that there is no structural evidence for substantial ground-state delocalisation between the cluster core and the pendant amine nitrogen centre in **4** and **5**, and the similarity of the bond parameters between the mono-cluster compounds and the analogous parameters in **6** argues against extended conjugation in the bis(cluster) system.

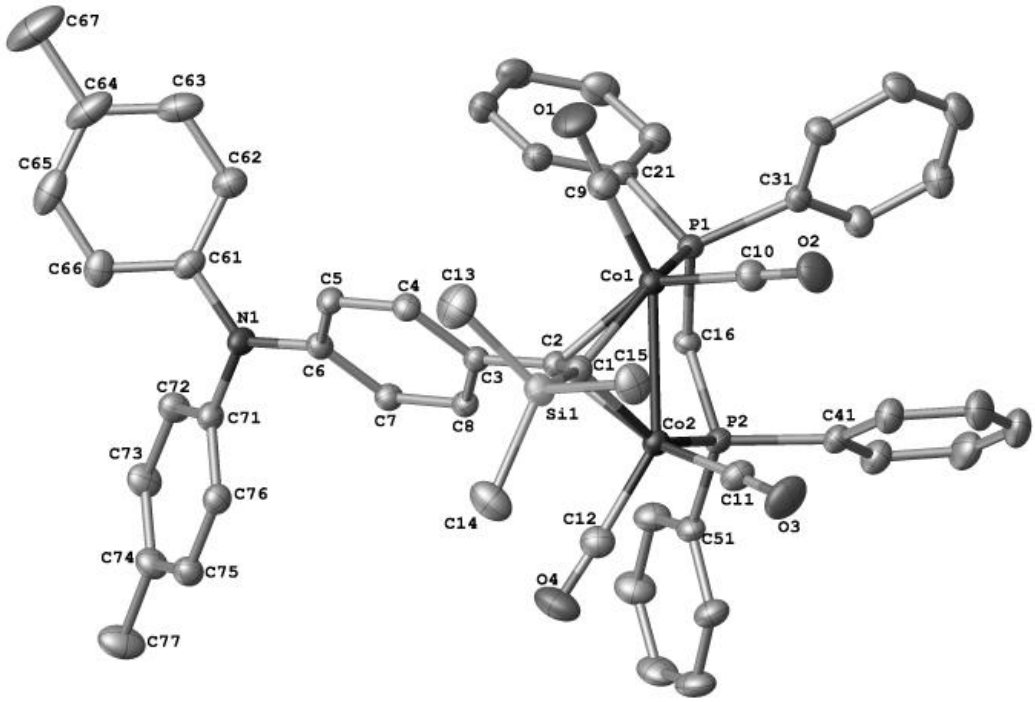


Figure 1 The molecular structure of **4**, showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): Co(1)-Co(2) 2.4884(5); Co(1)-P(1) 2.2211(5); Co(2)-P(2) 2.2161(6); Co(1)-C(1,2) 1.9674(19), 1.9924(18); Co(2)-C(1, 2) 1.9835(18), 1.9617(18); C(1)-C(2) 1.350(2); C(2)-C(3) 1.465(2); C(3)-C(4) 1.404(2); C(4)-C(5) 1.383(2); C(5)-C(6) 1.401(3); C(6)-C(7) 1.395(3); C(7)-C(8) 1.389(2); C(8)-C(3) 1.399(2); N(1)-C(6) 1.419(2); N(1)-C(61) 1.423(2); N(1)-C(71) 1.431(2); C(6)-N(1)-C(61) 120.51(15); C(6)-N(1)-C(71) 119.79(15); C(61)-N(1)-C(71) 119.55(15).

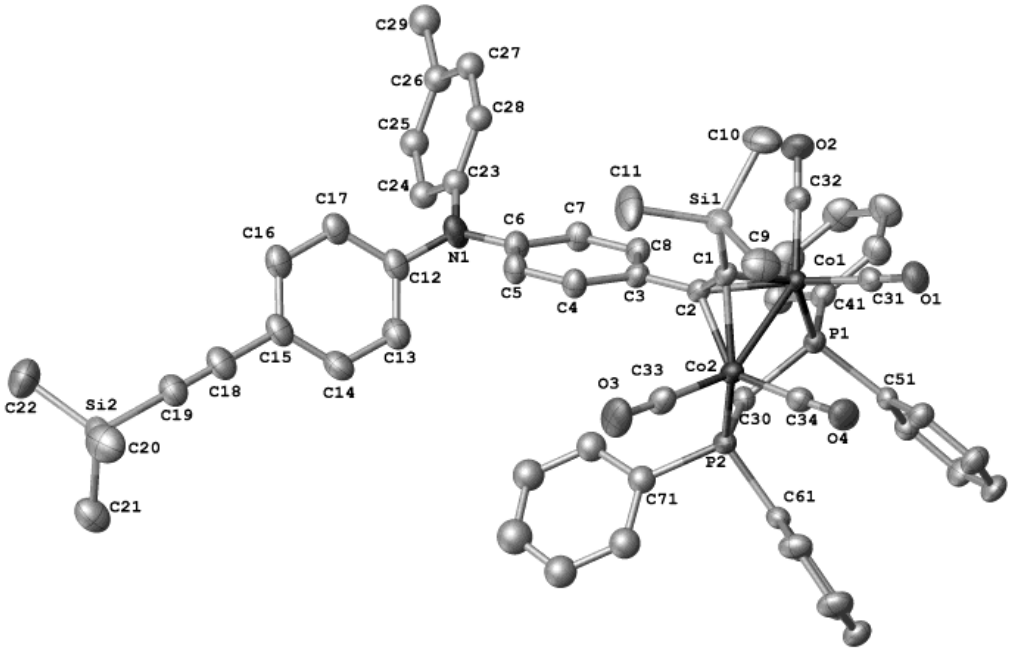


Figure 2 The molecular structure of **5**, showing the atom labelling scheme. Selected bond lengths (Å) and angles (°) (one component of a disordered model): Co(1)-Co(2) 2.4821(5); Co(1)-P(1) 2.2036(8); Co(2)-P(2) 2.2130(8); Co(1)-C(1,2) 1.975(3), 1.944(3); Co(2)-C(1, 2) 1.972(3), 1.989(3); C(1)-C(2) 1.351(4); C(2)-C(3) 1.475(4); C(3)-C(4) 1.399(4); C(4)-C(5) 1.387(4); C(5)-C(6) 1.398(4); C(6)-C(7) 1.391(4); C(7)-C(8) 1.393(4); C(8)-C(3) 1.396(4); N(1)-C(6) 1.413(4); N(1)-C(23) 1.380(5); N(1)-C(12) 1.414(4); C(6)-N(1)-C(23) 118.7(3); C(6)-N(1)-C(12) 119.8(3); C(23)-N(1)-C(12) 121.3(3).

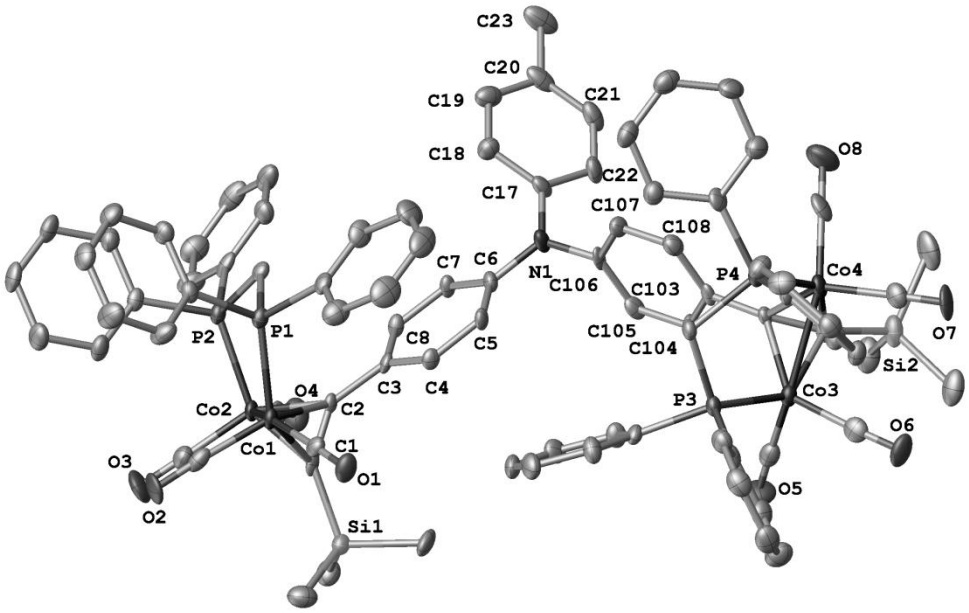


Figure 3 The molecular structure of **6** showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): Co(1)-Co(2) 2.4853(10); Co(1)-P(1) 2.2244(14); Co(2)-P(2) 2.1995(14); Co(1)-C(1,2) 1.976(5), 1.973(4); Co(2)-C(1, 2) 1.976(4), 1.966(4); C(1)-C(2) 1.351(6); C(2)-C(3) 1.461(6); C(3)-C(4) 1.405(6); C(4)-C(5) 1.383(6); C(5)-C(6) 1.402(6); C(6)-C(7) 1.390(7); C(7)-C(8) 1.387(6); C(8)-C(3) 1.398(6); Co(3)-Co(4) 2.4933(10); Co(3)-P(3) 2.2182(14); Co(4)-P(4) 2.2136(15); Co(3)-C(101,102) 1.981(5), 1.985(4); Co(4)-C(101, 102) 2.000(5), 1.964(5); C(101)-C(102) 1.353(6); C(102)-C(103) 1.468(6); C(103)-C(104) 1.407(7); C(104)-C(105) 1.376(6); C(105)-C(106) 1.390(7); C(106)-C(107) 1.372(7); C(107)-C(108) 1.401(7); C(108)-C(103) 1.376(6); N(1)-C(6) 1.405(6); N(1)-C(17) 1.430(6); N(1)-C(106) 1.439(6); C(6)-N(1)-C(106) 118.9(4); C(6)-N(1)-C(17) 122.1(4); C(106)-N(1)-C(17) 118.7(4).

Electrochemistry and spectroelectrochemistry The presence of redox active organic (NAr_3) and organometallic (Co_2C_2) moieties in **4**, **5** and **6** prompts investigation of the electrochemical response of these systems, which can be conveniently compared and contrasted with the electrochemical response of the ligands **2** and **3** and [Co_2(μ-$HC_2C_6H_4R$)$(CO)_4$(dppm)] model cluster complexes. The ethynyl-substituted triarylamines **2** and **3** each exhibit a single, electrochemically reversible oxidation wave in CH_2Cl_2 / 0.1 M $[NBu_4]PF_6$ solution at a platinum working electrode (Table 2). The half-wave potentials of these triarylamine derivatives varies modestly as a function of the peripheral groups, with substitution of one weakly electron-donating methyl group in **2** by a second, more electron-withdrawing trimethylsilylethynyl group in **3** resulting in a shift of $E_{1/2}$ by ca. +70 mV from +0.53 V (**2**) to +0.60 V (**3**). The clusters [Co_2(μ-$HC_2C_6H_4R$)$(CO)_4$(dppm)] undergo a one-electron oxidation and reduction, the redox potentials of which are also sensitive to the electron donating or withdrawing properties of the phenyl substitutent, R. For example, the oxidation wave shifts from ca. –0.10 V (R = NMe_2) to +0.23 V (R = H) and +0.29 V (R = NO_2) (vs ferrocene / ferrocenium in THF / 0.1 M $[NBu_4]PF_6$) [92]. In general, the chemical reversibility of these cluster-based redox processes improves at lower temperatures.

Compounds **4** and **5** feature both Co_2C_2 and triarylamine based redox centres, and unsurprisingly, each of these complexes exhibit two, one-electron oxidation waves, which are essentially chemically reversible at room temperature. By comparison with the data from **2**, **3** and the complexes [Co_2(μ-$HC_2C_6H_4R$)$(CO)_4$(dppm)], the first of these oxidation processes ($E_{1/2}$ = 0.04 V, **4**; 0.08 V, **5**) can be assigned to oxidation of the cluster, whilst the second wave ($E_{1/2}$ = 0.56 V, **4**; 0.60 V, **5**) can be attributed to

the triarylamine group; the relative potentials of these processes in **4** vs **5** follow the same substituent effects observed for **2** vs **3**.

At room temperature, electrochemical analysis of the bis(cluster) **6** was complicated by rapid passivation of the platinum electrode, and a film over the electrode surface was apparent by simple visual inspection. The chemical stability of the electrogenerated products improves at lower temperatures, and at –40°C the CV of **6** exhibits three reversible oxidation waves (Table 2), the first two of which ($E_{1/2}$ = 0.07, 0.17 V; $\Delta E_{1/2}$ = 100 mV) are assigned to sequential oxidation of the cluster cores and the third ($E_{1/2}$ = 0.63 V) to the triarylamine centre by comparison with the data from other complexes in Table 1, and results of spectroscopic investigations described below.

The observation of two separate oxidation events for the cluster based redox processes reflects the stability of $[\mathbf{6}]^{+}$ relative to **6** and $[\mathbf{6}]^{2+}$. The comproportionation constant, K_C, for the equilibrium

$$[\mathbf{6}] + [\mathbf{6}]^{2+} \overset{K_C}{\rightleftharpoons} 2\,[\mathbf{6}]^{+}$$

can be derived from the difference in the redox potentials, $\Delta E = |E_{1/2}(1)-E_{1/2}(2)|$, through the expression $K_C = \exp(\Delta EF/RT)$. As discussed elsewhere [21, 94-97] the thermodynamic stability of $[\mathbf{6}]^{+}$ relative to **6** and $[\mathbf{6}]^{2+}$ can be attributed to a number of factors which include solvation, ion-pairing, electrostatic effects and resonance / delocalisation. Of these various terms, only the latter relates to the concept of stabilisation arising from 'electronic interactions' between the remote cluster centres.

The observation of three distinct waves in the CV of **6** presents an interesting opportunity to address the role electrochemical and spectroelectrochemical methods can play in clarifying the electronic structure of compounds featuring multiple electroactive centres.

Although many interpretations of the significance of K_C have assumed a dominate contribution from delocalisation effects, Geiger and colleagues have presented a series of informative reminders of the significance of ion-pairing interactions in stabilising charged species, and the consequent effects that choice of supporting electrolyte can have on stabilising of intermediate charged species [98-100]. Table 2 summarises CV measurements of **4** and **6** conducted in CH_2Cl_2 / 0.1 M $[NBu_4][BAr^F_4]$ ($[BAr^F_4]^- = [B(C_6F_5)_4]^-$), and which emphasise the role weakly coordinating anions such as $[BAr^F_4]^-$ can play on stabilising charged species by maximising electrostatic (Coulombic or through space) effects.

Table 2 The electrochemical response of **2 - 6**

Complex	**Electrolyte**	**$E_{1/2}$ (1) / V**	**$E_{1/2}$ (2) / V**	**$\Delta E_{1/2}$ / mV**	**$E_{1/2}$ (amine)/ V**
2[a]	$[NBu_4]PF_6$				0.53
3[a]	$[NBu_4]PF_6$				0.60
4[b]	$[NBu_4]PF_6$	0.04	-	-	0.56
	$[NBu_4][BAr^F{}_4]$	0.05	-	-	0.63
5[b]	$[NBu_4]PF_6$	0.08	-	-	0.60
6[b]	$[NBu_4]PF_6$	0.07	0.17	100	0.63
	$[NBu_4][BAr^F{}_4]$	0.07	0.29	220	0.87

Conditions: 0.1 M electrolyte solutions in CH_2Cl_2, Pt electrode, scan rate 100 mV s^{-1}. Referenced to FcH/FcH^+ = 0 V. $[BAr^F{}_4]^-$ = $[B(C_6F_5)_4]^-$. [a] room temperature. [b] –40° C.

In the case of **4**, the cluster based oxidation takes place at essentially the same potential in both CH_2Cl_2 / 0.1M $[NBu_4]PF_6$ and CH_2Cl_2 / 0.1M $[NBu_4][BAr^F{}_4]$. However the amine oxidation in CH_2Cl_2 / 0.1M $[NBu_4][BAr^F{}_4]$ is some 70 mV more positive than in the $[NBu_4]PF_6$ electrolyte. This can be explained in terms of a simple electrostatic model; since the $[BAr^F{}_4]^-$ anion is less strongly associating than PF_6^- in CH_2Cl_2, the dication is less stabilised by ion-pairing interactions and further oxidation of $[\mathbf{4}]^+$ to $[\mathbf{4}]^{2+}$ is less favourable. In the case of the bis(cluster) compound **6**, changing the electrolyte anion from PF_6^- to $[BAr^F{}_4]^-$ results in an increased separation of the first two (cluster based) oxidation waves from $|E_{1/2}(1)-E_{1/2}(2)|$ = 100 mV

([NBu_4]PF_6) to 220 mV ([NBu_4][BAr^F_4]). The trication [**6**]$^{3+}$ is also less stablised in the [BAr^F_4]$^-$ containing electrolyte, and consequently the difference between the second and third oxidation processes |$E_{1/2}$(2)-$E_{1/2}$(3)| also increases from 460 mV in [NBu_4]PF_6 to 580 mV in [NBu_4][BAr^F_4]. Clearly, ion-pairing interactions with the electrolyte anion are playing a significant role in stabilising the charged states of these species, and the use of ΔE as a measure of the ground state interactions / delocalisation between the cluster centres and between the cluster centres and the amine moiety is not appropriate.

To further explore the nature of the redox products, and to investigate potential electronic interactions between the various electroactive components in **4** and **6**, we turned to IR and NIR spectroscopic methods. In the case of **4**, which offers more chemically reversible electrochemical behaviour at room temperature on platinum, the assignment of the first and second oxidation events to the cluster core and triarylamine, respectively, were confirmed by IR spectroelectrochemical studies. Upon one electron oxidation, a shift of ca. +45 cm^{-1} is observed in the ν(CO) frequencies (Figure 4), consistent with cluster oxidation.

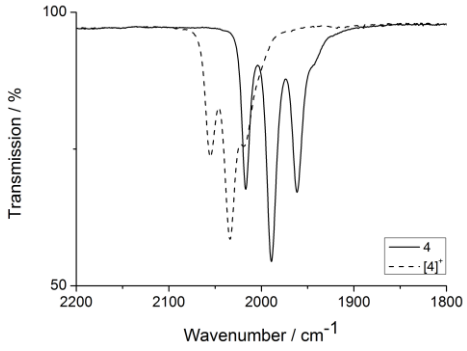


Figure 4. The spectroelectrochemically determined IR spectra of **4** and [**4**]$^+$ in CH_2Cl_2 / 0.1M $[NBu_4]PF_6$.

The poorer chemical stability of the redox products derived from bis(cluster) **6** and the rapid passivation of platinum electrodes observed in CV experiments precluded the further study of this compound using our room temperature spectroelectrochemical cell, which is fitted with a platinum gauze working electrode. However, chemical oxidation of **6** with $[Fe(\eta\text{-}C_5H_4COMe)Cp]PF_6$ ([FcAc]PF_6) [68] in CH_2Cl_2 at low temperature afforded solutions of [**6**]PF_6 and [**6**]$[PF_6]_2$, from which spectroscopic information could be obtained. Treatment of **6** with one equivalent of the oxidising agent gave [**6**]PF_6, the IR ν(CO) spectrum of which was characterised by a band pattern approximating a superposition of the spectra of **4** (2017m, 1989s, 1961m, 1942w cm^{-1}) and [**4**]$^+$ (2055m, 2034s, 2017m, 2007sh cm^{-1}) (Figure 5).

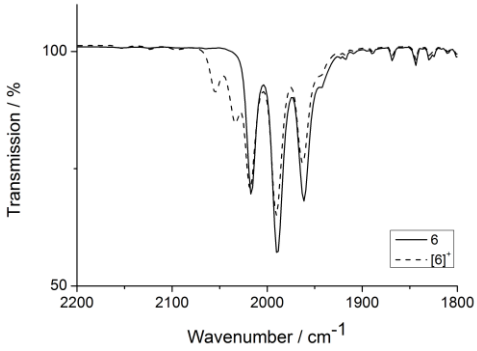


Figure 5. The IR ν(CO) spectra of **6** and [**6**]PF_6 (the latter obtained by stoichiometric oxidation of **6** with [FcAc]PF_6) in CH_2Cl_2.

This strongly supports a description of [**6**]$^+$ in terms of oxidation at one of the cluster moieties (bands at 2054w, 2033m, 2018sh (unresolved) cm^{-1}), with the radical cation

localised on the IR timescale. The very limited shift of the ν(CO) bands associated with the 'neutral' cluster in $[\mathbf{6}]^+$ (bands at 2018s, 1989s, 1961m, 1942w cm^{-1}) relative to those in the parent cluster **6** (2016m, 1989s, 1960m, 1941w cm^{-1}) indicates little ground state delocalisation between the two cluster moieties. Upon treatment of $[\mathbf{6}]PF_6$ with a second equivalent of oxidant, the dication $[\mathbf{6}][PF_6]_2$ is formed and the ν(CO) band pattern (bands at 2058m, 2037s, 2020m, 2007sh cm^{-1}) evolves towards a pattern similar to that observed for $[\mathbf{4}]^+$ (2055m, 2034s, 2017m, 2007sh cm^{-1}). The IR spectrum of $[\mathbf{6}][PF_6]_2$ is therefore consistent with the presence of two oxidised, but non-interacting, cluster moieties (Figure 6).

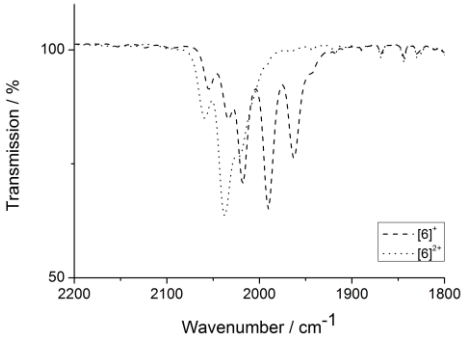


Figure 6 The IR ν(CO) spectra of $[\mathbf{6}]PF_6$ and $[\mathbf{6}][PF_6]_2$ (obtained by stoichiometric oxidation of **6** with $[FcAc]PF_6$) in CH_2Cl_2.

Turning to NIR spectroscopy, a new electronic transition is observed in $[\mathbf{4}]^+$ at 7920 cm^{-1} (1260 nm) / ε = 1590 M^{-1} cm^{-1}. A very similar transition is observed in the NIR spectrum of $[\mathbf{6}]PF_6$ (8020 cm^{-1} (1250 nm) / ε = 2260 M^{-1} cm^{-1}), although on the basis of this spectroscopic data alone it is not possible to unambiguously determine if the band envelope also conceals a cluster-to-cluster intervalence charge transfer band.

However, further oxidation of [**6**]PF_6 to [**6**][PF_6]$_2$ results not in a collapse of the low energy feature, but rather an increase in the band intensity and a small shift to higher energy (8950 cm^{-1} (1120 nm) / ε 4320 $M^{-1}cm^{-1}$). In addition, the spectrum of the simple tolyl substituted cluster [{$Co_2(CO)_4$(dppm)}{μ-($Me_3SiC_2C_6H_4$-4-Me)}]$^+$ ([**7**]$^+$, obtained by spectroelectrochemical oxidation of **7** in CH_2Cl_2 / 0.1 M [NBu_4]PF_6) contains a weak band in the same region (8240 cm^{-1} (1210 nm) / ε 350 $M^{-1}cm^{-1}$). On the basis of the IR and NIR data we conclude that the cluster centres in [**6**]$^{n+}$ are electronically independent, and that the low energy electronic absorption band is associated with electronic transitions within the [Co_2C_2]$^+$ cluster core.

Conclusion Simplified synthetic protocols have been developed for [$Co_2(CO)_6$(dppm)] (**1**), and the trimethylsilylethynyl-substituted triarylamines [N(C_6H_4-4-C≡C$SiMe_3$)(C_6H_4Me-4)$_2$] (**2**) and [N(C_6H_4-4-C≡C$SiMe_3$)$_2$(C_6H_4Me-4)] (**3**). Reaction of **1** with **2** or **3** gives the anticipated Co_2C_2 tetrahedrane clusters [{$Co_2(CO)_4$(dppm)}{μ-(Me_3SiC_2-4-C_6H_4)N(C_6H_4Me-4)$_2$}] (**4**), [Co_2{μ-Me_3SiC_2-4-C_6H_4N(C_6H_4-4-C≡C$SiMe_3$)(C_6H_4Me-4)}$(CO)_4$(dppm)] (**5**) and [{$Co_2(CO)_4$(dppm)}$_2${μ-(Me_3SiC_2-4-C_6H_4)$_2$N(C_6H_4Me-4)}] (**6**). Structural parameters determined by single crystal X-ray diffraction indicate the Co_2C_2 cluster cores to be in essentially identical electronic environments, and there is no structural evidence for ground state delocalisation either between the amine nitrogen and the cluster core in **4** and **5**, nor between the clusters in **6**. Electrochemical and spectroelectrochemical analysis reveals the cluster centres to be oxidised at less positive potentials than the triarylamine moiety, and that the clusters in **6** are oxidised sequentially in two separate one-electron processes. The difference in cluster oxidation potentials in **6** is sensitive to the nature of the supporting electrolyte anion, varying from |$E_{1/2}$(1)-

$E_{1/2}(2)$| = 100 mV in CH_2Cl_2 / 0.1M $[NBu_4]PF_6$ to 220 mV in CH_2Cl_2 / 0.1M $[NBu_4][BAr^F{}_4]$. The IR ν(CO) spectrum of $[\mathbf{6}]^+$ clearly indicates the localised (on the IR time scale) electronic structure of this species, with the cluster centres acting independently; there is no evidence for bridge-mediated cluster-cluster interactions. The NIR spectra of the cluster radicals $[\mathbf{4}]^+$ and $[\mathbf{6}]^{n+}$ (n = 1, 2) feature almost identical low energy electronic transitions, but there is no indication of a new transition in $[\mathbf{6}]^+$ that can be attributed to a cluster-to-cluster IVCT style transition. A similar, albeit weak, band is also observed in the model compound (8240 cm^{-1} (1210 nm) / ε = 350 M^{-1} cm^{-1}) which suggests this low energy transition is associated with the oxidised dicobalt dicarbon tetrahedrane cluster core. On the basis of all of the available data it must be concluded that the cluster centres in [**6**] are electronically independent, and that $[\mathbf{6}]^+$ represents a cluster based Class I Robin and Day mixed valence system.

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Supporting Information Available Details of the preparation and characterisation of **7**, figure showing the IR spectra of **7** and $[\mathbf{7}]^+$, figure showing the NIR spectra of $[\mathbf{4}]^+$, $[\mathbf{6}]^+$, $[\mathbf{6}]^{2+}$ and $[\mathbf{7}]^+$.

References

1. K.D. Demadis, C.M. Hartshorn and T.J. Meyer (2001). *Chem. Rev.* **101**, 2655.

2. Y. Lu, R. Quardokus, C.S. Lent, F. Justaud, C. Lapinte and S.A. Kandel (2010). *J. Am. Chem. Soc.* **132**, 13519.

3. D.M. D'Alessandro and F.R. Keene (2008). *Pure Appl. Chem.* **80**, 1.

4. D.M. D'Alessandro and F.R. Keene (2006). *Chem. Rev.* **106**, 2270.

5. D.M. D'Alessandro and F.R. Keene (2006). *Chem. Soc. Rev.* **35**, 424.

6. C. Creutz (1983). *Prog. Inorg. Chem.* **30**, 1.

7. B.S. Brunschwig, C. Creutz and N. Sutin (2002). *Chem. Soc. Rev.* **31**, 168.

8. A. Inagaki and M. Akita (2010). *Coord. Chem. Rev.* **254**, 1220,

9. A.J. Esswein, A.S. Veige and D.G. Nocera (2005). *J. Am. Chem. Soc.* **127**, 16641.

10. A.F. Heyduk and D.G. Nocera (2001). *Science* **293**, 1639.

11. N. Sutin, B.S. Brunschwig and C. Creutz (2003). *J. Phys. Chem. B* **107**, 10687.

12. D.M. Adams, L. Brus, C.E.D. Chidsey, S. Creager, C. Creutz, C.R. Kagan, P.V. Kamat, M. Lieberman, S. Lindsay, R.A. Marcus, R.M. Metzger, M.E. Michel-Beyerle, J.R. Miller, M.D. Newton, D.R. Rolison, O. Sankey, K.S. Schanze, J. Yardley and X. Zhu (2003). *J. Phys. Chem. B* **107**, 6668.

13. W. Kaim (2011). *Inorg. Chem.* **50**, 9752.

14. K. Costuas and S. Rigaut (2011). *Dalton Trans.* **40**, 5643.

15. J. Maurer, B. Sarkar, B. Schwederski, W. Kaim, R.F. Winter and S. Zalis (2006). *Organometallics* **25**, 3701.

16. W.Y. Man, J.-L. Xia, N.J. Brown, J.D. Farmer, D.S. Yufit, J.A.K. Howard, S.H. Liu and P.J. Low (2011). *Organometallics* **30**, 1852.

17. M.A. Fox, B. Le Guennic, R.L. Roberts, D.A. Brue, D.S. Yufit, J.A.K. Howard, G. Manca, J.-F. Halet, F. Hartl and P.J. Low (2011). *J. Am. Chem. Soc.* **133**, 18433.

18. P. Aguirre-Etcheverry and D. O'Hare (2010). *Chem. Rev.* **110**, 4839.

19. M.I. Bruce and P.J. Low (2004). *Adv. Organomet. Chem.* **50**, 179.

20. A. Heckmann and C. Lambert (2012). *Angew. Chem. Int. Ed.* **51**, 326.

21. P.J. Low and N.J. Brown (2010). *J. Cluster Sci.* **21**, 235.

22. G. Canzi and C.P. Kubiak (2011). *Small* **7**, 1967.

23. J.C. Goeltz, E.E. Benson and C.P. Kubiak (2010). *J. Phys. Chem. B* **114**, 14729.

24. S.D. Glover, J.C. Goeltz, B.J. Lear and C.P. Kubiak (2010). *Coord. Chem. Rev.* **254**, 331.

25. J.C. Goeltz, C.J. Hanson and C.P. Kubiak (2009). *Inorg. Chem.* **48**, 4763.

26. S.D. Glover, B.J. Lear, J.C. Salsman, C.H. Londergan and C.P. Kubiak (2008). *Proc. Trans. R. Soc. A* **366**, 177.

27. P.A. Brooksby, N.W. Duffy, A.J. McQuillan, B.H. Robinson and J. Simpson (1999). *J. Organomet. Chem.* **582**, 183.

28. C.J. McAdam, J.J. Brunton, B.H. Robinson and J. Simpson (1999). *J. Chem. Soc., Dalton Trans.* 2487.

29. G.H. Worth, B.H. Robinson and J. Simpson (1992). *Organometallics* **11**, 3863.

30. S. Clement, L. Guyard, A. Khatyr, M. Knorr, Y. Rousselin, M.M. Kubicki, Y. Mugnier, S. Richeter, P. Gerbier and C. Strohmann (2012). *J. Organomet. Chem.* **699**, 56.

31. A. Albinati, F, Balzano, F.F, de Biani, P. Leoni, G, Manca, L. Merchetti, S, Rizzato, G.U. Barretta and P. Zanello (2010). *Inorg. Chem.* **49**, 3714.

32. R.D. Adams and B. Qu (2000). *Organometallics* **19**, 4090.

33. R.D. Adams and B. Qu (2001). *J. Organomet. Chem.* **620**, 303.

34. R.D. Adams, O.-S. Kwon, B. Qu and M.D. Smith (2001). *Organometallics* **20**, 5225.

35. R.D. Adams, B. Qu and M.D. Smith (2001). *J. Organomet. Chem.* **637-639**, 514.

36. R.D. Adams and B. Qu (2001). *J. Organomet. Chem.* **619**, 271.

37. R.D. Adams, B. Qu and M.D. Smith (2002). *Organometallics* **21**, 3867.

38. R.D. Adams, B. Qu, M.D. Smith and T.A. Albright (2002). *Organometallics* **21**, 2970.

39. R.D. Adams, B. Qu and M.D. Smith (2002). *Organometallics* **21**, 4847.

40. A. Arnanz, M.-L. Marcos, S. Delgado, J. González-Velasco and C. Moreno (2009). *Dalton Trans.* 168.

41. A. Albinati, F. F. de Biani, P. Leoni, L. Marchetti, M. Pasquali, S. Rizzato and P. Zanello (2005). *Angew. Chem. Int. Ed.* **44**, 5701.

42. R.S. Dickson and P.J. Fraser (1974). *Adv. Organomet. Chem.* **12**, 323.

43. M.L. Marcos, M.J. Macazaga, R.M. Medina, C. Moreno, J.A. Castro, J.L. Gomez, S. Delgado and J. Gonzalez-Velásco (2001). *Inorg. Chim. Acta* **312**, 249.

44. C. Moreno, M.-L. Marcos, G. Dominguez, A. Arnanz, D.H. Farrar, R. Teeple, A. Lough, J. Gonzalez-Velasco and S. Delgado (2001). *J. Organomet. Chem.* **631**, 19.

45. R.M. Medina, C. Moreno, M.L. Marcos, J.A. Castro, F. Benito, A. Arnanz, S. Delgado, J. González-Velasco and M.J. Macazaga (2004). *Inorg. Chim. Acta* **357**, 2069.

46. D. Osella, L. Milone, C. Nervi and M. Ravera (1998). *Eur. J. Inorg. Chem.* 1473.

47. C.J. McAdam, N.W. Duffy, B.H. Robinson and J. Simpson (1996). *Organometallics* **15**, 3935.

48. B.H. Dana, B.H. Robinson and J. Simpson (2002). *J. Organomet. Chem.* **648**, 251.

49. A. Arnanz, C. Moreno, M.-L. Marcos, J. González-Velasco and S. Delgado (2007). *Eur. J. Inorg. Chem.* 5215.

50. A. Arnanz, M.-L. Marcos, C. Moreno, D.H. Farrar, A.J. Lough, J.O. Yu, S. Delgado and J. González-Velasco (2004). *J. Organomet. Chem.* **689**, 3218.

51. L.-A. Hore, C.J. McAdam, J.L. Kerr, N.W. Duffy, B.H. Robinson and J. Simpson (2000). *Organometallics* **19**, 5039.

52. N. Duffy, J. McAdam, C. Nervi, D. Osella, M. Ravera and B. Robinson, J. Simpson (1996). *Inorg. Chim Acta* **247**, 99.

53. P.J. Low, R. Rousseau, P. Lam, K.A. Udachin, G.D. Enright, J.S. Tse, D.D.M. Wayner and A.J. Carty (1999). *Organometallics* **18**, 3885.

54. M.A. Fox, M.A.J. Paterson, C. Nervi, F. Galeotti, H. Puschmann, J.A.K. Howard and P.J. Low (2001). *Chem. Commun.* 1610.

55. B. Le Guennic, K. Costuas, J.-F. Halet, C. Nervi, M.A.J. Paterson, M.A. Fox, R.L. Roberts, D. Albesa-Jové, H. Puschmann, J.A.K. Howard and P.J. Low (2005). *C.R. Chemie* **8**, 1883.

56. K. Onitsuka, N. Ohara, F. Takei and S. Takahashi (2006). *Dalton Trans.* 3693.

57. K. Onitsuka, N. Ohara, F. Takei and S. Takahashi (2008). *Organometallics* **27**, 25.

58. R.L. Roberts, T. Schwich, T.C. Corkery, M.P. Cifuentes, K.A. Green, J.D. Farmer, P.J. Low, T.B. Marder, M. Samoc and M.G. Humphrey (2009). *Adv. Mater.* **21**, 2318.

59. G. Grelaud, O. Cador, T. Roisnel, G. Argouarch, M.P. Cifuentes, M.G. Humphrey and F. Paul (2012). *Organometallics*, DOI 10.1021/om2006358.

60. L.S. Chia and W.R. Cullen (1975). *Inorg. Chem.* **14**, 482.

61. I.J.S. Fairlamb, A.R. Kapdi and A.F. Lee (2004). *Org. Lett.* **6**, 4435.

62. J.D. Woollins (2003), *Inorganic Experiments*, 2nd Ed, Wiley-VCH, Verlag Gmbh, pp 91.

63. N. Miyaura and A. Suzuki (1993). *Org. Synth., Coll. Vol. 8*, 532.

64. D.R. Coulson (1990). *Inorg. Synth.* **28**, 107.

65. Y. Chang and T.J. Chow (2009). *Tetrahedron* **65**, 9626.

66. K. Sakamaki, J. Ohshita, A. Kunai, H. Nakao, A. Adachi and K. Okita (2001). *Appl. Organomet. Chem.* **15**, 939.

67. M.J. Plater and T. Jackson (2003). *Tetrahedron* **59**, 4687.

68. N.G. Connelly and W.E. Geiger (1996). *Chem. Rev.* **96**, 877.

69. M. Krejčík, M. Daněk and F. Hartl (1991). *J. Electroanal. Chem.* **317**, 179.

70. Sheldrick, G.M. (1996). SADABS: University of Goettingen, Germany

71. O.V.Dolomanov, L.J.Bourhis, R.J.Gildea, J.A.K.Howard and H.Puschmann (2009). *J. Appl. Cryst*. **42**, 339.

72. G. M. Sheldrick (2008). *Acta Cryst., Sect. A* **64**, 112.

73. Z. Ning and H. Tian (2009). *Chem. Commun.* 5483.

74. P.J. Low, M.A.J. Pateron, H. Puschmann, A.E. Goeta, J.A.K. Howard, C. Lambert, J.C.. CHerryman, D.R Tackley, S. Leeming and B. Brown (2004). *Chem. Eur. J.* **10**, 83.

75. P.J. Low, M.A.J. Paterson, D.S. Yufit, J.A.K. Howard, J.C. Cherryman, D.R. Tackley, R. Brook and B. Brown (2005). *J. Mater. Chem.* **5**, 2304.

76. P.J. Low, M.A.J. Paterson, A.E. Goeta, D.S. Yufit, J.A.K. Howard, J.C. Cherryman, D.R. Tackley and B. Brown (2004). *J. Mater. Chem.* **14**, 2516.

77. Y. Shirota and H. Kageyama (2007). *Chem. Rev.* **107**, 953.

78. D. Maiti, B.P. Fors, J.L. Henderson, Y. Nakamura and S.L. Buchwald (2011). *Chem. Sci.* **2**, 57.

79. J.F. Hartwig (2008). *Acc. Chem. Res.* **41**, 1534.

80. R. Chinchilla and C. Nájera (2011). *Chem. Soc. Rev.* **40**, 5084.

81. C. Xu, J.-F. Gong and Y.-J. Wu (2007). *Tetrahedron Lett.* **48**, 1619.

82. G.Y. Li, G. Zheng and A.F. Noonan (2001). *J. Org. Chem.* **66**, 8677.

83. C.V. Reddy, J.V. Kingston and J.G. Verkade (2008). *J. Org. Chem.* **73**, 3047.

84. U. Christmann, D.A. Pantazis, J. Benet-Buchholz, J.E. McGrady, F. Maseras and R. Vilar (2006). *J. Am. Chem. Soc.* **128**, 6376.

85. B.U. Maes, K.T.J. Loones, G.L. Lemiere and R.A. Dommisse (2003). *Synlett*, 1822.

86. B.H. Lipshutz and H. Ueda (2000). *Angew. Chem. Int. Ed.* **39**, 4492.

87. U. Christmann, R. Vilar, A.J.P. White and D.J. Williams (2004). *Chem. Commun.*1294.

88. S.R. Suresh and K.C.K. Swamy (2009). *Tetrahedron Lett.* **50**, 6004.

89. D.A. Pratt, G.A. DiLabio, L. Valgimigli, G.F. Pedulli and K.U. Ingold (2002). *J. Am. Chem. Soc.* **124**, 11085.

90. X. Liu and S. Zhang (2011). *Synlett* 1137.

91. N.S. Nandurkar, M.J. Bhanushali, M.D. Bhor and B.M. Bhanage (2007). *Tetrahedron Lett.* **48**, 6573.

92. T.J. Snaith, P.J. Low, R. Rousseau, H. Puschmann and J.A.K. Howard (2001). *Dalton Trans.* 292.

93. A.N. Sobolev, V.K. Belsky, I.P. Romm, N.Yu. Chernikova and E.N. Guryanova (1985). *Acta Cryst. Sect. C* **C41**, 967.

94. D.M. D'Alessandro and F.R. Keene (2004). *Dalton Trams.* 3950.

95. J.E. Sutton and H.E. Taube (1981). *Inorg. Chem.* **20**, 3125.

96. D.E. Richardson and H. Taube (1983). *J. Am. Chem. Soc.* **105**, 40.

97. D.E. Richardson and H. Taube (1984). *Coord. Chem. Rev.* **60**, 107.

98. F. Barrière, N. Camire, W.E. Geiger, U.T. Mueller-Westerhoff and R. Sanders (2002). *J. Am. Chem. Soc.* **124**, 7262.

99. F. Barrière and W.E. Geiger (2006). *J. Am. Chem. Soc.* **128**, 3980.

100. W.E. Geiger and F. Barrière (2010). *Acc. Chem. Res.* **43**, 1030.